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IN SITU FTIR STUDY OF CO₂ REDUCTION ON
POLYCRYSTALLINE PLATINUM IN ACID SOLUTIONS

by

H. Huang, C. Fierro, D. Scherson and E. Yeager

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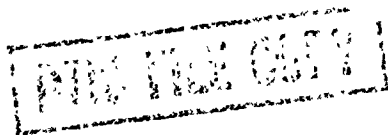
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ABSTRACT

The reduction of CO₂ on polycrystalline Pt in 0.1 M HClO₄ has been investigated with in situ Fourier Transform Infrared Reflection Absorption Spectroscopy and electrochemical techniques. Both methods have provided clear evidence that the reaction proceeds at potentials at which adsorbed hydrogen is also present on the surface. Based on the spectroscopic information it has been concluded that linear and bridge-bonded forms of adsorbed CO are the only detectable reduction products with the latter achieving saturation coverage well before the peak associated with linearly bonded CO reaches maximum intensity. Two similar CO bands have also been observed by other authors for CO₂ reduction on Pt in 0.5 M H₂SO₄ using the EMIRS technique. The low energy band, however, was ascribed by these authors to CO bound on a three-fold site.

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INTRODUCTION

During the last few decades considerable effort has been devoted to the electrochemical conversion of CO_2 to more useful hydrocarbon and other organic species.¹⁻³ Most of these studies have been carried out in aqueous solutions using bare metals as electrode materials^{4-8,11-26} as well as a growing variety of molecular species either adsorbed on the electrode surface or in the solution phase.²⁷⁻³¹ Despite much effort, however, no consensus has yet been reached regarding basic aspects of these reduction reactions including mechanistic pathways and the way in which these are influenced by the nature of the metal or the electrocatalyst.

REDUCTION OF CO_2 ON Pt ELECTRODES: BRIEF BACKGROUND

According to most reports in the literature, the reduction of CO_2 on Pt electrodes has been found to occur in the hydrogen adsorption region to generate an adsorbed species denoted generically as "reduced CO_2 ",^{2,4-7} which can be oxidized at significantly more positive potentials. In fact, a clear identification of the precise nature of this species (as either adsorbed CO or adsorbed COH) has been the subject of much heated controversy. Evidence in support of COH has been obtained by Shlpakov et al.,⁸ using ^{14}C -labelled Na_2CO_3 for experiments involving a platinized Pt electrode in 0.5 M H_2SO_4 . According to these authors, such an adsorbed species is capable of displacing three hydrogen atoms and undergo a three-electron oxidation. Similar COH species have also been postulated in the electrochemical oxidation of methanol by Willsan et al.,⁹ based on differential electrochemical mass spectroscopy measurements. *In situ* IR spectroscopy, however, has failed to reveal species other than adsorbed CO for the same system (*vide infra*).¹⁰

A single species in two different adsorption geometries has been postulated to explain (among other experimental observations) the double

oxidation peaks observed in cyclic voltammetry experiments for CO₂ reduction on Pt electrodes.^{6-8,11,12} There exists some discrepancy in the literature regarding whether the two adsorption geometries are sensitive to the coverage of the CO₂ reduction product or the potential at which the reduction is carried out, or both.

Perhaps the best evidence in support of CO as the "reduced CO₂" is provided by the preliminary work of Beden et al. who employed Electrochemical Modulated Infrared Spectroscopy (EMIRS), to examine CO₂ reduction on Pt in 0.5 M H₂SO₄.¹³ In agreement with the presence of the same adsorbate on two different sites was the occurrence of a strong spectral feature at 2060 cm⁻¹ and a weaker one at 1865 cm⁻¹ when CO₂ was reduced in the hydrogen adsorption region, which these authors attributed to CO bonded to a one-fold, and a three-fold site, respectively.

The main aim of this work is to identify the reduction products of CO₂ reduction on a polycrystalline Pt electrode in 0.1 M HClO₄ solutions by *in situ* Fourier Transform Infrared Reflection Absorption Spectroscopy, FTIRRAS³². Perchlorate, unlike bisulfate or sulfate ions, display only very weak specific adsorption in the potential region of interest and therefore the effects associated with coadsorbed species other than atomic hydrogen can be greatly minimized. It may be noted that CO₂ may contain CO as a trace impurity and therefore the possibility exists that part or all of the CO observed does not originate from CO₂ reduction. In order to circumvent this difficulty the CO₂ was produced *in-situ* with the electrode pushed close to the optical window, by oxidizing the adsorbed CO formed during exposure of the bare platinum to the CO₂-saturated solution at a potential of -0.2 V vs SCE. As will be shown, CO₂ undergoes reduction in the hydrogen adsorption region to yield adsorbed CO on both bridge and top sites. These results are in qualitative agreement with those reported by Beden et al.¹³ for Pt in 0.5 M H₂SO₄ using EMIRS, and afford

strong evidence that the so-called "reduced CO₂" reported in prior work,^{2,4,6,25} indeed corresponds to adsorbed CO.

EXPERIMENTAL

All measurements were conducted in 0.1 M HClO₄ at -20°C. The solutions were prepared with Ultrex grade HClO₄ (Baker) and ultrapurified water.³³ High purity CO₂ (99.99%) and N₂ were obtained from Matheson.

The electrochemical cell used in these experiments was the same as that described in earlier studies^{34,35} and involves the combined use of a polished polycrystalline Pt electrode of ellipsoidal shape (1.7 cm²) and a 60° beveled CaF₂ dove prism window. All potentials are reported against a saturated calomel electrode, SCE. Voltammetry curves were recorded in the *in situ* IR cell with the electrode pulled back from the optical window. For the actual spectroscopic measurements two different procedures were used. The electrode was first polarized either in the hydrogen adsorption (Method I) or in the double layer region (Method II) in a solution saturated with CO₂ for a given period of time and then pushed against the window while polarized at that same potential.

FTIR spectra in the region between 1100 and 3500 cm⁻¹ were obtained with an IR/98 Michelson-Genzel interferometer system (IBM Instruments, Inc.) with a resolution of 8 cm⁻¹. A total of about 400 interferometric scans were accumulated with the electrode polarized at a specified potential. The voltage was then stepped to the desired value and a new spectrum involving the same number of scans was collected without disturbing the overall cell arrangement. The spectra shown in the figures represent the difference between the first spectrum obtained at a reference potential, E_r, and second spectrum obtained at a sample potential, E_s, i.e., $-\Delta R/R = 1 - R(E_s)/R(E_r)$, where R(E_s) and R(E_r) are the reflectances at the sample and reference potentials, respectively.

RESULTS AND DISCUSSION

Curve A, Fig. 1 (solid line) shows a typical voltammogram of Pt in a CO₂-saturated 0.1 M HClO₄ solution obtained in the *in situ* IR cell with the electrode away from the window. Two main differences can be observed between this voltammogram and that recorded in the same electrolyte saturated with N₂ (not shown in this figure): a depressed hydrogen adsorption region and an anodic peak at ca. +0.4 V. As shown in curve B in the same figure (dotted line), these effects could be greatly enhanced when the potential was held at -0.2 V for 2 min and the scan then resumed proceeding first in the negative direction. These results are in good agreement with those reported by Marcos et al^{7,12,25,26} and provide evidence that the feature at +0.4 V may be attributed to the oxidation of the so-called "reduced CO₂" generated at the more cathodic potentials as proposed by other authors.^{2,6,7,17}

A series of experiments were conducted using Method I, with the Pt electrode first polarized for 2 min at potentials in the region between +0.2 and -0.2 V, E_r , before the electrode was pushed close to the window. After a spectrum was recorded, the potential was stepped to +0.6 V, E_s , (positive to the anodic peak in the voltammogram) and a new spectrum was acquired. No features could be observed for the difference spectra obtained for $E_r \geq 0.0$ V indicating that within the sensitivity of the present IR technique no reaction takes place (see Fig. 2). This is consistent with additional electrochemical experiments of the type shown in Fig. 1, in which the Pt electrode was polarized at potentials in the range between 0.0 and +0.2 V in a CO₂-saturated solution. In this case the peak at +0.4 V could not be detected during the anodic scan after holding the potential at these values for 2 min. This behavior is unlike that observed for Pt exposed to a CO-saturated solution which yielded a characteristic CO oxidation peak at 0.4 V after being polarized

in the same potential range for the same length of time.³⁶

Three clearly defined peaks could be observed for the difference spectra obtained at -0.1 and -0.2 V (see Fig. 2). The negative peaks at 2048-2052 cm^{-1} and 1811-1817 cm^{-1} can be attributed to linear and bridge-bonded CO^{37,38}, respectively, whereas the positive peak at 2345 cm^{-1} corresponds to solution phase CO₂. The presence of two CO peaks is in qualitative agreement with those of Beden et al.¹³ who also reported two forms of adsorbed CO in their EMIRS studies.

The fact that the difference spectra at $E_r \geq 0.0$ V are featureless strongly suggests that the CO detected in the spectra at -0.1 and -0.2 V originates from CO₂ reduction and not from CO impurities in the CO₂. Further evidence in support of this view was obtained from an essentially identical experiment in which the solution phase CO₂ was removed by bubbling N₂ for 30 min after the initial exposure of the Pt to a CO₂-saturated solution with the electrode polarized at -0.2 V for 10 min. The difference spectrum observed after stepping the potential to +0.6 V shown in Curve A, Fig. 3 displays the same features as those in Fig. 2. The potential was then stepped back to -0.2 V to reduce the CO₂ formed and again a new difference spectrum with the same features as those in Fig. 2 was obtained using that acquired at +0.6 V as the reference (see Curve B). The smaller intensity of the peaks for this last curve suggests that the CO₂ trapped in the thin layer may not be completely reduced during the waiting period used before the collection of the spectrum (~2 min), as the difference appears far too large to be explained by losses due to diffusion of the trapped CO₂ away from the thin layer. An essentially mirror image of Curve B was obtained after stepping the potential to +0.6 V to oxidize the adsorbed CO (Curve C, Fig. 3).

Chang and Weaver³⁸ have examined the change in the stretching frequency of linearly bonded CO, $\nu_{\text{CO}}^{\text{L}}$, as a function of potential and coverage for CO

adsorbed by the dosing technique on Pt(100) in 0.1 M HClO₄. In this procedure, the Pt electrode is exposed to very dilute solutions of CO to achieve the desired coverage. It was found by these authors that for low CO coverages (0.28 and below) $\nu_{\text{CO}}^{\text{t}}$ increases as the potential is shifted towards negative values in the range between 0.0 and -0.25 V vs. SCE. Although at first glance the same conclusions may be made by comparing the difference spectra at -0.1 V and -0.2 V displayed in Fig. 2, the reproducibility of the gap for independent experiments may not be sufficient to ascertain that the integrated intensities of the CO₂ peaks (and thus the absolute CO coverage) were the same in the two experiments.

The FTIRRAS experiments using Method I were designed to monitor only adsorbed products of CO₂ reduction. Further insight into the reaction process was obtained from measurements employing Method II with the Pt electrode pushed close to the optical window at +0.2 V in a CO₂-saturated 0.1 M HClO₄ solution. At this potential a reference spectrum was acquired, and then the potential was stepped to each of the five sample potentials in the sequence 0.0, -0.1, -0.15, -0.20 and -0.25 V without moving the electrode from the optical window. At each of these potentials a sample spectrum was recorded. Two positive peaks and one negative peak were observed when the potential was adjusted to -0.10 V. The positive peaks correspond to the formation of adsorbed CO in both linear and bridge-bonded states, while the negative peak corresponds to the consumption of CO₂ trapped in the thin layer between the optical window and the Pt electrode. No other well-defined absorption bands were observed in the region between 1100 and 3500 cm⁻¹ to indicate the presence of any other possible products or intermediates of CO₂ reduction, such as formic acid and/or methane.

The difference spectra for the region between 1500 and 2500 cm⁻¹ obtained

in these measurements are shown in Fig. 4. As indicated the peak at 1805 cm^{-1} appears at -0.1 V and does not change either in frequency or intensity at more cathodic potentials in the range examined. The band at $2029 - 2052\text{ cm}^{-1}$, however, changes in both frequency and intensity as the potential is adjusted from -0.10 to -0.20 V and remains the same as the potential reaches more cathodic values. This indicates that the bridge-bonded CO is saturated first as the reaction proceeds in the potential range examined. One possible explanation for this effect may be found in the much higher affinity of CO for bridge rather than linear sites in this potential range. This would be in agreement with semi-empirical quantum mechanical calculations for CO adsorbed on a Pt electrode,³⁹ which indicate that CO favors bridge over linear bonding as the potential is made more negative. The shift of the linear CO band to higher frequencies as the potential is shifted more negative may reflect a complicated interplay between the change in potential and the increase in coverage.^{32,38,40-42} For Pt(100), for example, the first factor causes a higher or lower frequency shift depending on the coverage³⁸, whereas the increased change in coverage at a constant potential always leads to higher frequency values.^{38,41,42}

From an overall perspective, the ability of polycrystalline Pt to reduce CO_2 in the acid media selected for these studies may introduce complications in the analysis of CO stripping-type experiments.^{38,42,43} In such measurements the Pt surface is first exposed to a CO-saturated solution at a potential negative to the onset of CO oxidation, E_{ads} , for a period of time long enough to reach full coverage. The electrode is then stepped to a potential sufficiently positive, E_{ox} , for a short period of time so as to oxidize partially the CO layer and then stepped back to E_{ads} . In this fashion it is possible to obtain submonolayer coverages of CO in a fairly controlled fashion. If E_{ads} , however, is within the hydrogen adsorption region,^{38,42,43} part or all of the CO_2

produced during the oxidation of adsorbed CO may undergo reduction. According to the results presented in this paper, this will generate additional adsorbed CO and thus contribute to the overall spectra. Although the conclusions made in this work are valid for polycrystalline Pt surfaces similar effects have been found for Pt(110) and Pt(100).⁴⁴

SUMMARY

CO₂ reduction on a polycrystalline Pt electrode in 0.1 M HClO₄ occurs at potentials within the hydrogen adsorption region yielding adsorbed linear and bridge-bonded CO as the only detectable products. This is consistent with the preliminary EMIRS results in 0.5 M H₂SO₄ reported earlier in the literature.

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REFERENCES

- (1) Vassiliev, Yu. B.; Bagotzky, V. S.; Osetrova, N. V.; Khazova, O. A. and Mayorova, N. A. *J. Electroanal. Chem.* 1985, 189, 271.
- (2) Vassiliev, Yu. B.; Bagotzky, V. S.; Khazova, O. A. and Mayorova, N. A. *J. Electroanal. Chem.* 1985, 189, 295.
- (3) Vassiliev, Yu. B.; Bagotzky, V. S.; Osetrova, N. V. and Mikhailova, A. A. *J. Electroanal. Chem.* 1985, 189, 311.
- (4) Giner, J. *Electrochim. Acta*, 1964, 9, 63.
- (5) Breiter, M. W. *J. Electroanal. Chem.* 1968, 19, 131.
- (6) Baruzzi, A. M.; Leiva, E. P. M. and Giordano, M. C. *J. Electroanal. Chem.* 1983, 158, 103.
- (7) Marcos, M. L.; Vara, J. M.; Gonzalez-Velasco, J. and Arvia, A. J. *J. Electroanal. Chem.* 1987, 224, 189.
- (8) Shlpakov, A. V.; Andreev, U. N. and Kazarinov, V. E. *Elektrokhimiya*, 1989, 25, 73.
- (9) Willsan, J.; Wolter, O. and Heitbaum, J. J. *Electroanal. Chem.* 1985, 185, 163.
- (10) Beden, B.; Lamy, C.; Bewick, A. and Kanimatsu, K. *J. Electroanal. Chem.* 1981, 121, 343.
- (11) Biegler, T. J. *J. Phys. Chem.* 1968, 72, 1571.
- (12) Marcos, M. C.; Gonzalez-Velasco, J.; Vara, J. M.; Giordano, M. C. and Arvia, A. J. *J. Electroanal. Chem.* 1989, 270, 205.
- (13) Beden, B.; Bewick, A.; Razaq, M.; Weber J. J. *Electroanal. Chem.* 1982, 139, 203.
- (14) Brummer, S. B.; Cahill, K. J. *J. Electroanal. Chem.* 1969, 21, 463.
- (15) Stalder, C. J.; Chao, S.; and Wrighton, M. S. *J. Am. Soc. Chem.* 1984, 106, 3673.
- (16) Frese, Jr., K. W. and Leach, S. J. *Electrochem. Soc.* 1985, 132, 259.
- (17) Baruzzi, A. M.; Leiva, E. P. M. and Giordano, M. C. *J. Electroanal. Chem.* 1985, 189, 257.
- (18) Hori, Y.; Kikuchi, K.; Murata, A. and Suzuki, S. *Chem. Lett.* 1986, 897.
- (19) Cook, R. L.; MacDuff, R. C. and Sammells, A. F. *J. Electrochem. Soc.* 1987 134, 2375.
- (20) Ikeda, S.; Takagi, T. and Ito, K. *Bull. Chem. Soc. Jpn.* 1987, 60, 2517.

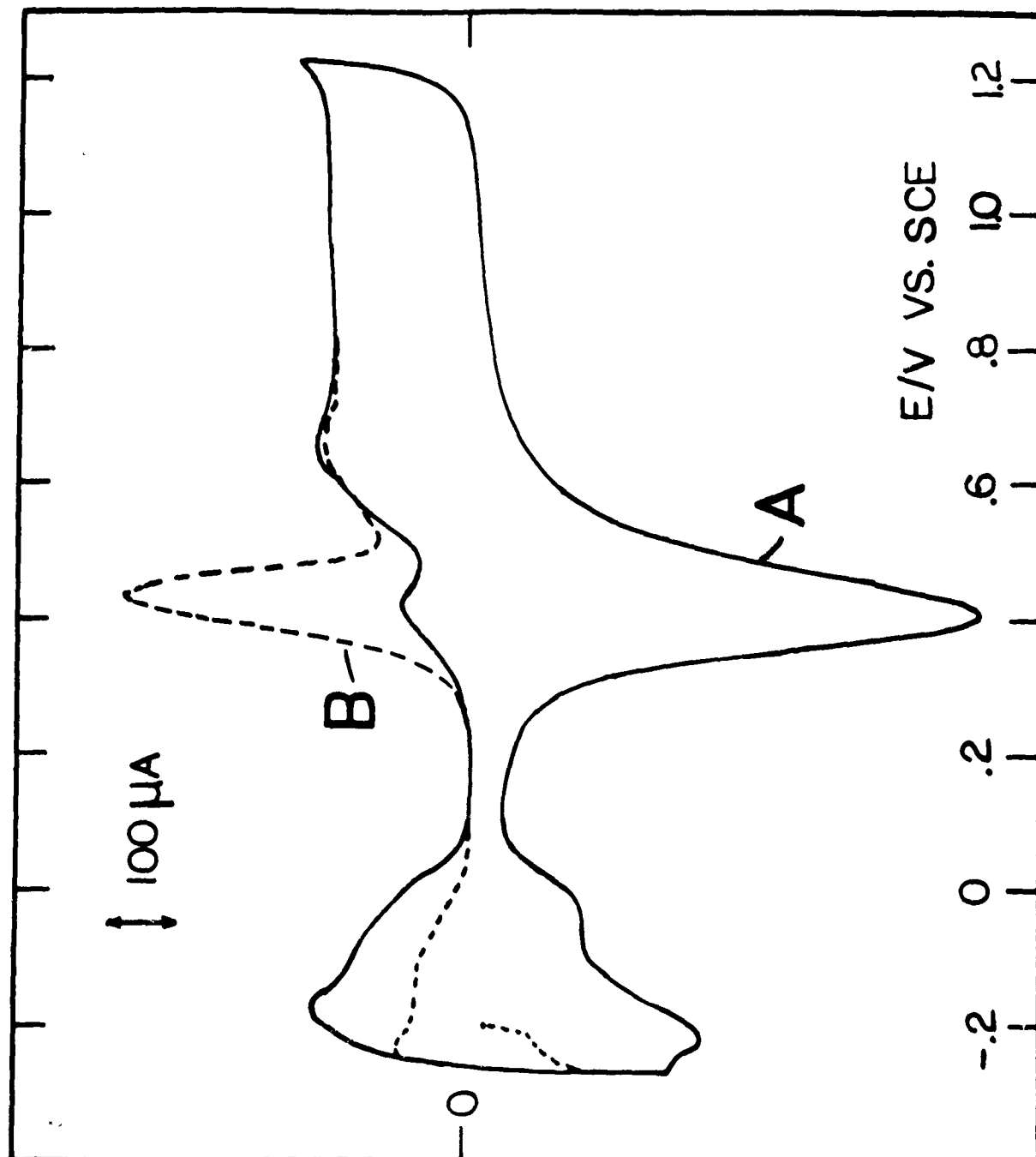
- (21) Cook, R. L.; MacDuff, R. C. and Sammells, A. F. *J. Electrochem. Soc.* 1988, 135, 1320.
- (22) Dewulf, D. C.; Jin, T. and Bard, A. J. *J. Electrochem. Soc.* 1989, 136, 1686.
- (23) Cook, R. L.; MacDuff, R. C.; Sammells, A. F. *J. Electrochem. Soc.* 1989, 136, 1982.
- (24) Azuma, M.; Hashimoto, K.; Hiramoto, M.; Watanabe, M. and Sakata, T. *J. Electrochem. Soc.* 1990, 137, 1772.
- (25) Marcos, M. L.; Gonzalez-Velasco, J.; Giordano, M. C. and Arvia, A. J. *J. Electroanal. Chem.* 1990, 281, 257.
- (26) Marcos, M. L.; Gonzalez-Velasco, J.; Vara, J. M.; Giordano, M. C. and Arvia, A. J. *J. Electroanal. Chem.* 1990, 287, 99.
- (27) Lieber, C. M. and Lewis, N. S. *J. Am. Chem. Soc.* 1984, 106, 5033.
- (28) Kapusta, S. and Hackerman, N. J. *J. Electrochem. Soc.* 1984, 131, 1511.
- (29) Beley, M.; Collin, J. -P.; Ruppert, R. and Sauvage, J. -P. *J. Am. Chem. Soc.* 1986, 108, 7461.
- (30) Christensen, P. A.; Hamnett, A. and Muir, A. V. G. *J. Electroanal. Chem.* 1988, 241, 361.
- (31) Fujihira, M.; Hirata, Y. and Suga, K. *J. Electroanal. Chem.* 1990, 292, 199.
- (32) Ashley, K.; Pons, S. *Chem. Rev.* 1988, 88, 673.
- (33) The water was purified by means of a reverse osmosis distillation system reported by Gilmont, R.; Silvis, S. *J. Am. Lab.* 1974, 6, 46, and modified by Dr. Cahan, B.
- (34) Bae, I. T.; Xing, X.; Liu, C. C. and Yeager E. B. *J. Electroanal. Chem.* 1990, 284, 335.
- (35) Sasaki, T.; Bae, I. T. and Scherson, D. A. *Langmuir*, 1990, 6, 1234.
- (36) Kita, H.; Shimazu, K. and Kunimatsu, K. *J. Electroanal. Chem.* 1988, 241, 163.
- (37) Leung, L.-W.; Chang, S.-C. and Weaver, M. J. *J. Chem. Phys.* 1989, 90, 7426.
- (38) Chang, S. -C. and Weaver, M. J. *J. Phys. Chem.* 1990, 94, 5095.
- (39) Mahandru, S. P. and Anderson, A. B. *J. Phys. Chem.* 1989, 93, 2044.
- (40) Kunimatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G. and Philpott, M. R. *Surf. Sci.* 1985, 158, 596.

- (41) Severson, M. W.; Russell, A.; Campbell, D.; Russell, J. W. *Langmuir*, 1987, 3, 202.
- (42) Chang, S. -C. and Weaver, M. J. *Surf. Sci.* 1990, 230, 222.
- (43) Chang, S. -C.; Leung, L. -W.; Weaver, M. J. *J. Phys. Chem.* 1989, 93, 5341.
- (44) Nikolic, B. Z.; Huang, H.; Gervasio, D.; Lin, A.; Fierro, C.; Adzic, R. R. and Yeager, E. B. *J. Electroanal. Chem.* in press.

FIGURE CAPTIONS

- Fig. 1. Voltammograms of a Pt electrode in a CO_2 -saturated 0.1 M HClO_4 solution in the *in situ* IR cell with the Pt electrode pulled back from the optical window (A, solid line), and after holding at -0.2 V for 2 min with the scan resumed proceeding first in the negative direction (B, dotted line). Scan rate: 100 mV/s. Electrode area: 1.7 cm^2 .
- Fig. 2. Potential difference FTIRRAS spectra obtained in a CO_2 -saturated 0.1 M HClO_4 solution for $E_s = +0.6$ V and $E_r = +0.2, +0.1, 0.0, -0.1, -0.2$ V, before and after the anodic peak in the voltammogram, respectively. The Pt electrode was pushed close to the optical window at each E_r after holding at this value for 2 min.
- Fig. 3. A: Potential difference FTIRRAS spectrum obtained in a N_2 -saturated 0.1 M HClO_4 solution with only adsorbed CO on the Pt electrode surface resulting from prior exposure of the Pt to a CO_2 -saturated solution at -0.2 V for 10 min, $E_r = -0.2$ V and $E_s = +0.6$ V.
B: reduction of CO_2 generated in A, $E_r = +0.6$ V and $E_s = -0.2$ V.
C: reoxidation of adsorbed CO formed in B, $E_r = -0.2$ V and $E_s = +0.6$ V.
- Fig. 4. Potential difference FTIRRAS spectra obtained in a CO_2 -saturated 0.1 M HClO_4 solution with +0.2 V as reference potential and a series of potentials from 0.0 to -0.25 V as sample potentials. The Pt electrode was pushed close to the optical window at +0.2 V and a reference spectrum collected. The potential was then stepped to each of five sample potentials in the sequence 0.0, -0.1, -0.15, -0.20 and -0.25 V without moving the electrode from the optical window.

fig. 1.



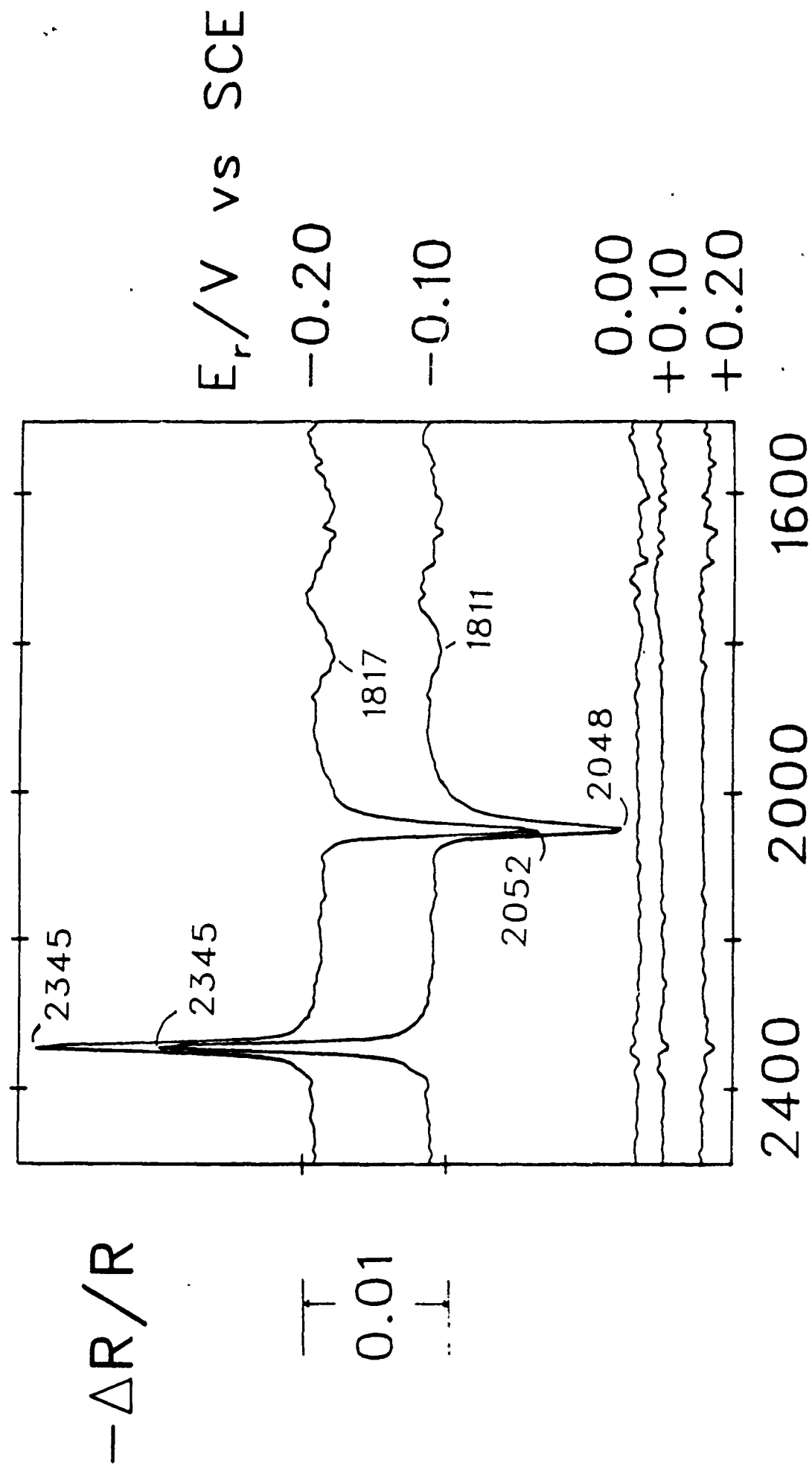


fig. 2.

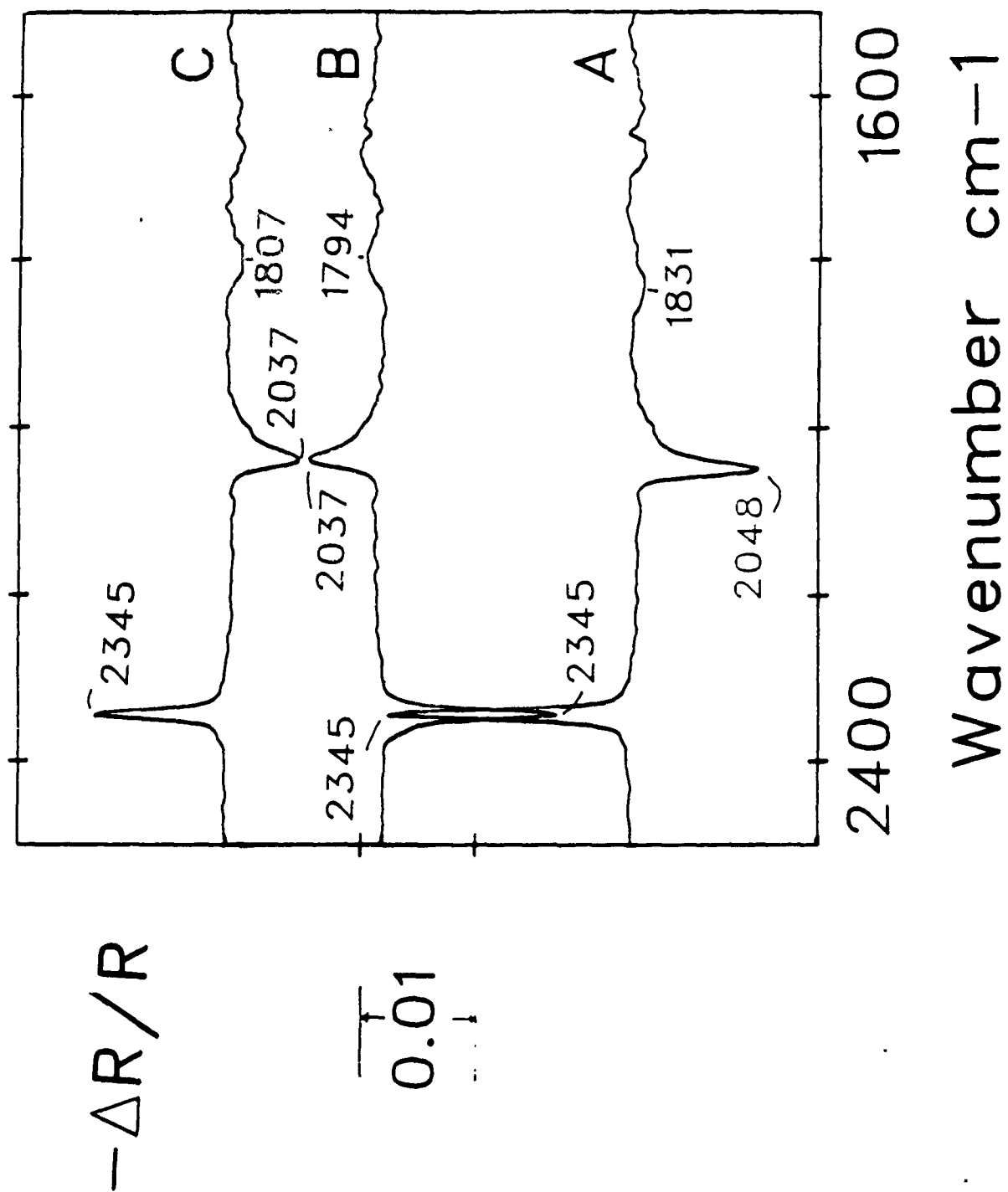


fig. 3.

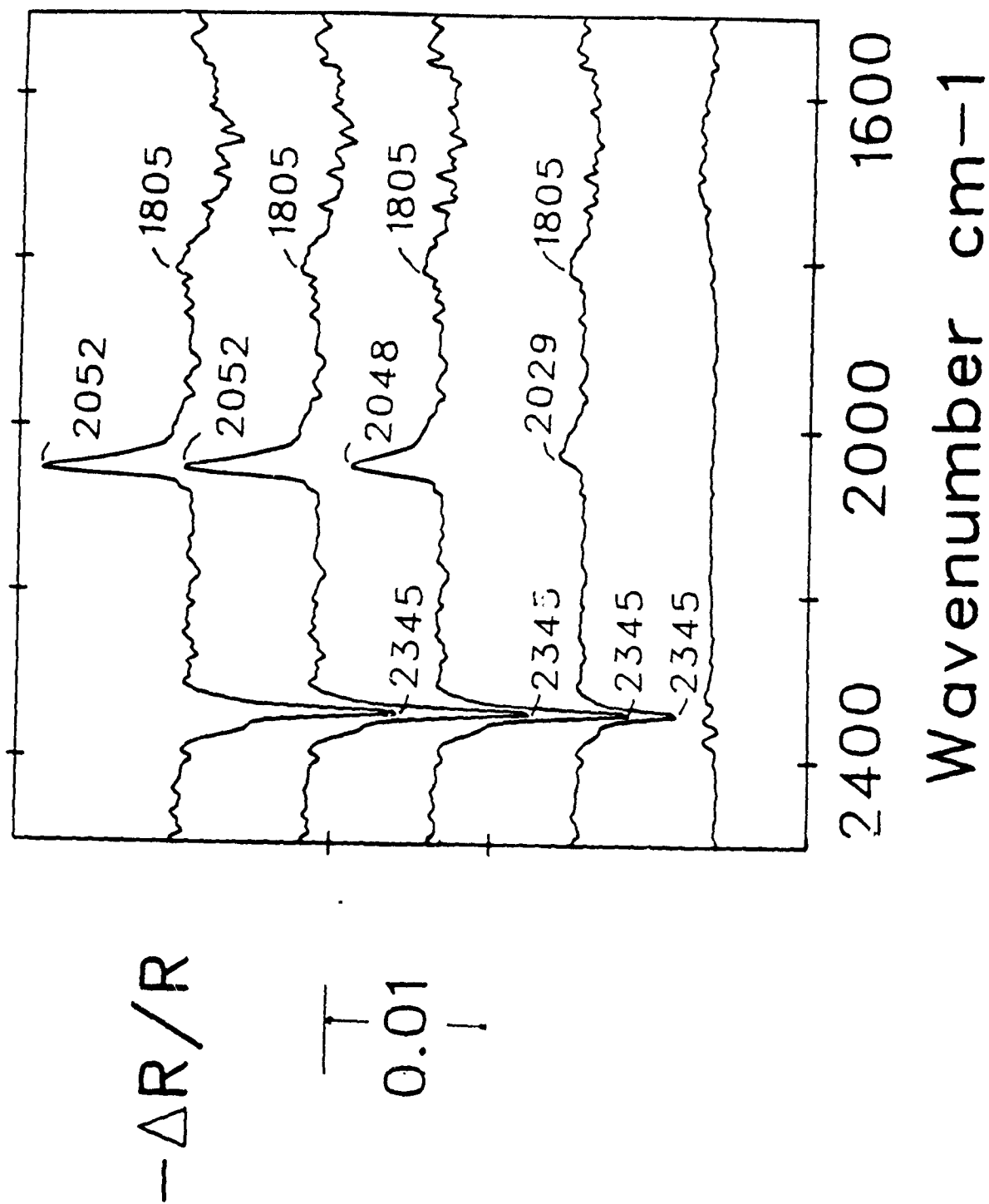


Fig. 4.